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Dynamic Mechanical and Dielectric Properties of Modified Surface Chitosan/Natural Rubber Latex

(Sifat Mekanik Dinamik dan Dielektrik Permukaan Chitosan yang Diubahsuai/Lateks Getah Asli)

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ABSTRACT

Biodegradable polymeric films, obtained from chitosan/natural rubber latex (CS/NRL) blends with different compositions, have been prepared by wetting process. The blends were characterized by dynamic mechanical thermal analysis (DMTA) and found that the CS/NRL blends are thermodynamically incompatible. This is evident from the presence of two glass transitions, corresponding to CS and NRL phases in the blend. The mechanical properties of the CS/NRL blends were improved with increasing the amount of chitosan and after surface treatment with sulphuric acid due to the sulfonate ionic interaction. The dielectric properties was determined using Precision LCR meter in the frequency range 75 kHz up to 30 MHz. After CS/NRL surface treatment with sulphuric acid at high content of chitosan showed the highest dielectric constant. The surface properties of the CS/NRL blend films before and after surface treatment were confirmed by atomic force microscopy (AFM), respectively.

Keywords: Biopolymer; chitosan; dielectric properties; natural rubber; surface modification

ABSTRAK

Penggunaan filem terbiourai yang diperoleh daripada campuran (CS/NRL) lateks getah asli/ kitosan dengan komposisi yang berbeza, telah disediakan secara proses basah. Campuran dicirikan menggunakan teknik analisis haba mekanik dinamik (DMTA) dan mendapati bahawa campuran CS/NRL semula jadi tidak serasi. Ini adalah jelas daripada kewujudan dua peralihan kaca, yang sesuai dengan fasa CS dan NRL dalam adunan. Sifat mekanik campuran CS/NRL telah dipertingkatkan dengan meningkatkan jumlah kitosan dan selepas rawatan permukaan menggunakan asid sulfurik berlaku interaksi ionik sulfonat. Sifat dielektrik ditentukan menggunakan LCR ketepatan meter dalam kekerapan julat 75 kHz sehingga 30 MHz. Selepas rawatan permukaan CS/NRL dengan asid sulfurik pada kandungan yang tinggi daripada kitosan menunjukkan berlakunya pembentukan malar dielektrik yang tertinggi. Sifat permukaan CS/NRL menggabungkan filem sebelum dan selepas rawatan permukaan telah disahkan masing-masing oleh mikroskop berkuat-kuasa atom (AFM).

Kata kunci: Getah asli; kitosan; permukaan pengubahsuaian; polimer-Bio ditawarkan; sifat dielektrik

INTRODUCTION

Natural rubber (NR) has excellent mechanical properties but it likes any other polymers which are composed with highly unsaturated chain that is susceptible to oxidative degradation. A number of publications deal with incorporation of hydrophilic biopolymer such as chitosan with NR to obtain higher permeability (Ismail et al. 2011; Sapuan et al. 2011) and selectivity as well as good thermal stability (Clarizia et al. 2004; Kittur et al. 2005). Generally, chitosan is biocompatible and biodegradable with wide range of applications in cosmetic, pharmaceutical and medical industries. More importantly, in reactivity point of view, it possesses two nucleophilic moieties namely the primary amine (-NH2) and hydroxyl (-OH) groups (Wanichapichart et al. 2009). Incorporation of chitosan with NR has been done via solution blend (homogeneous reaction) and dry blend (heterogeneous reaction). Solution blend of chitosan with NR was found that the both of permeation flux and separation selectivity of water-isopropanol mixtures were increased with increasing chitosan content (Kittur et al. 2005; White et al. 2010).

In this study, the membrane was prepared from incorporation of chitosan with NR to improve their properties as well as the conductivity of NR film. The main propose of this research was the development of bio-materials for electrolyte membrane. The effects of sulfuric acid membrane surface treatment on the physical and electrical properties were also investigated.

METHODS

High ammonia concentrated NR latex (NRL) with dry rubber content (DRC) 60.1% by weight was purchased from Chalong Latex Industry, Songkla, Thailand. Chitosan (deacetylation degree of 85% with average molecular weight is 500000 g/mol) was purchased from Seafresh Industry Public Co., Ltd. Three gram of chitosan was dissolved in 97 g of acetic acid solution (10% v/v) by stirring for 48 h and filtering to remove undissolved matter.

The chitosan solution was directly mixed with NRL (DRC = 40% by weight in the presence with stabilizer 0.5% by weight) by varying weight ratio between chitosan solution and NRL as illustrated in Table 1.

TABLE 1. Composition of polymer blend film between chitosan and NRL

Sample	Weight (g)	
	Chitosan	NRL
CA3NS0590	90	10
CA3NS0592	92	8
CA3NS0594	94	6
CA3NS0596	96	4
CA3NS0598	98	2

The mixture was poured into petri dish and followed by drying at room temperature. The polymer films were neutralized by immersing in 4% (w/v) NaOH solution and washing with water until the waste washing water pH reached closed to 7.0. The resulting polymer films were left to dry at room temperature in a dust free chamber.

The dynamic mechanical properties of the membrane were performed using dynamic mechanical thermal analyser (DMTA; Model-V, supplied by Rheometric Scientific). The shape of test sample was rectangular, 25 mm long, 10 mm wide and 1.5 mm thick. The single cantilever mode of deformation was used under the test temperature range from -100 to 200°C with a heating rate of 3°C/min; the test frequency being 1 Hz. The cooling process was achieved through liquid nitrogen.

Surface morphology of the membrane was studied using atomic force microscope (AFM), Park System XE70. The surface roughness average (R_a) and root mean squared (R_q) were calculated from Nanoscope software by using (1) and (2):

$$R_a = \frac{1}{n}\sum_{j=1}^{n}|Z_j|, \quad (1)$$

$$R_q = \sqrt{\frac{1}{n}\sum_{j=1}^{n}Z_i^2}, \quad (2)$$

where Z_j is the difference between the height and the mean plane current and n is number of points. Dielectric measurements were carried out in the frequency range 75 kHz up to 30 MHz by using Precision LCR meter (Agilent 4285A).

RESULTS AND DISCUSSION

DYNAMIC MECHANICAL THERMAL ANALYSIS (DMTA)

The properties obtained from the dynamic mechanical thermal analysis are the storage modulus (E'), loss modulus (E") and loss tangent (tan δ) of the biopolymeric blending film is recorded as a function of temperature from -100 to 200°C and showed in Figure 1. In Figure 1, the storage modulus is found to increase with incorporation of chitosan with NR below the glass transition temperature. The incorporation of NR has improved the stiffness of the chitosan around the glassy region. The damping property (tan δ) which is the ratio of the dynamic loss modulus to the dynamic storage modulus is found to decrease with incorporation of Chitosan with NR. Since chitosan is rigid with it dissipates energy and thus the height of damping peak increases. The tan δ peaks observed correspond to the glass transition temperature (T_g) of the matrix. The T_g of the obtained bio-blend increased indicates good interaction between NR and chitosan.

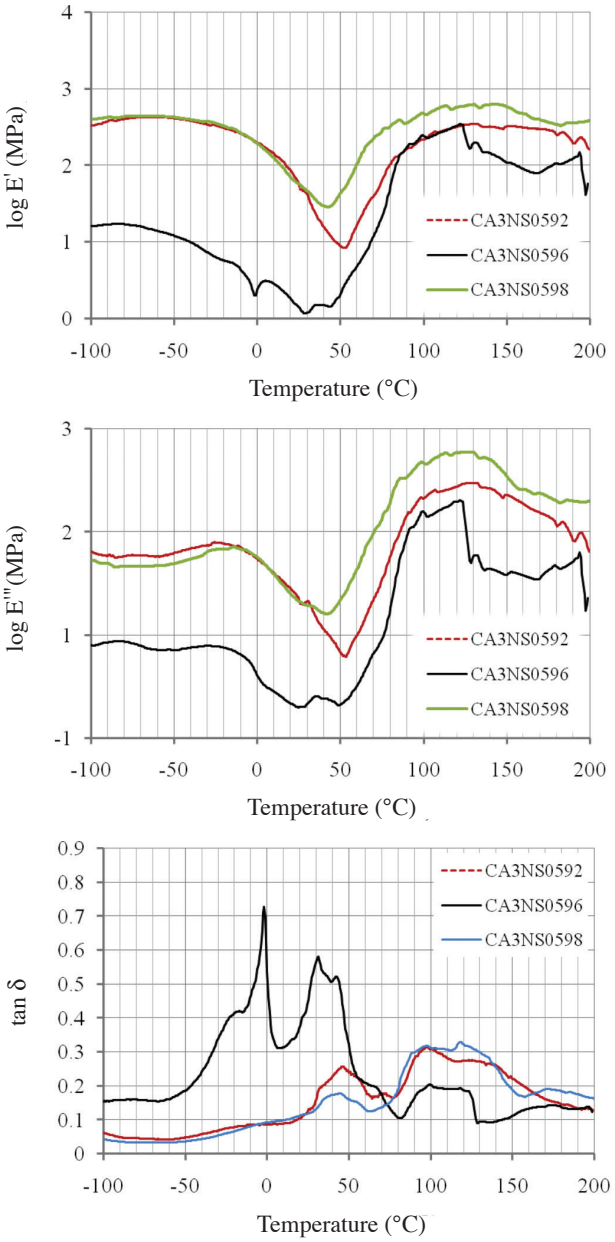

FIGURE 1. Dynamic mechanical thermal properties of chitosan incorporated with NR with difference compositions (a) tan δ, (b) log E" and (c) log E' versus temperature

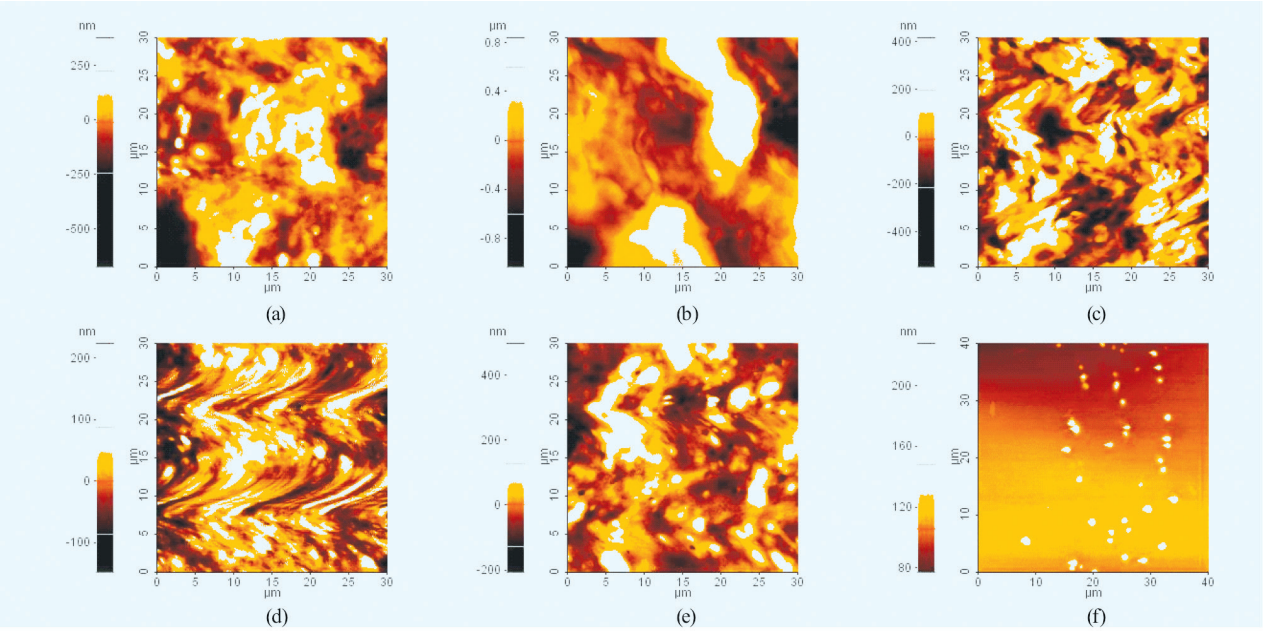

FIGURE 2. AFM topology images of chitosan (f) and chitosan blending with natural rubber CA3NS0590 (a) 8% CA3NS0592 (b) CA3NS0594 (c) CA3NS0596 (d) and CA3NS0598 (e)

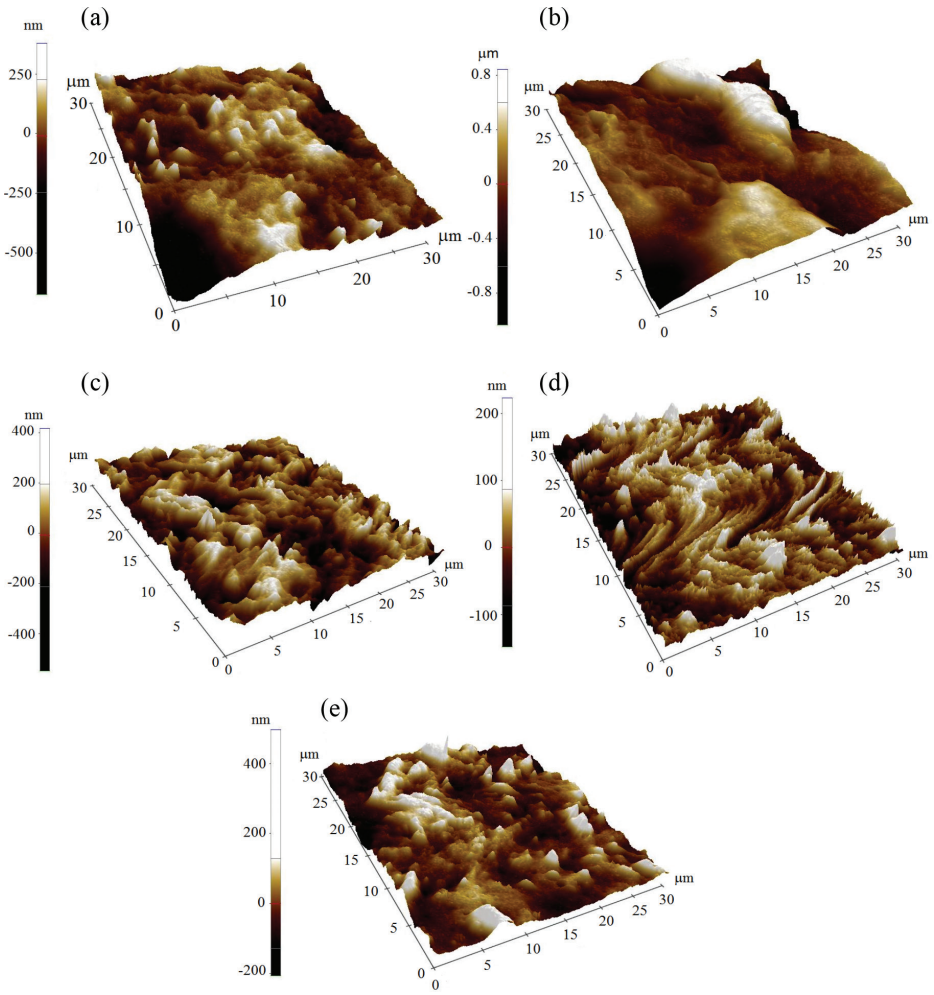

FIGURE 3. AFM 3-dimension images of chitosan blending with natural rubber CA3NS0590 (a) 8% CA3NS0592 (b) CA3NS0594 (c) CA3NS0596 (d) and CA3NS0598 (e)

SURFACE PROPERTIES

The AFM micrographs in Figures 2 and 3 clearly show that the chitosan incorporated with NR formed the aggregate structure with high surface roughness. The surface roughness average (R_a) and root mean squared (R_q) were calculated and shown in Table 2.

TABLE 2. Surface roughness values of membrane on mica substrate

Membrane	R_q (nm)	R_a (nm)
CA3NS0590	87	121
CA3NS0592	235	307
CA3NS0594	84	104
CA3NS0596	35	44
CA3NS0598	50	65
Chitosan	10	12

DIELECTRIC PROPERTIES

The permittivity and dielectric loss of polymer films were measured over the frequency range from 75 kHz up to 30 MHz at room temperature. The dielectric constant of the polymer film with higher content of chitosan increased as shown in Figure 4. Blending of chitosan with NR, dense NR film was formed and covered chitosan particles resulted in the film conductivity is decreased. The NR phase was removed after immersing the polymer film in sulfuric acid solution. The dielectric properties increased with increasing the immersing time as shown in Figure 5 as well as the dielectric loss as shown in Figure 6. The chitosan blending with high content of NR, sulfonate ionic interaction was occurred in NR phase after immersing the polymer film in sulfuric acid for longer time. Both of interfacial polarization and conductivity are increased.

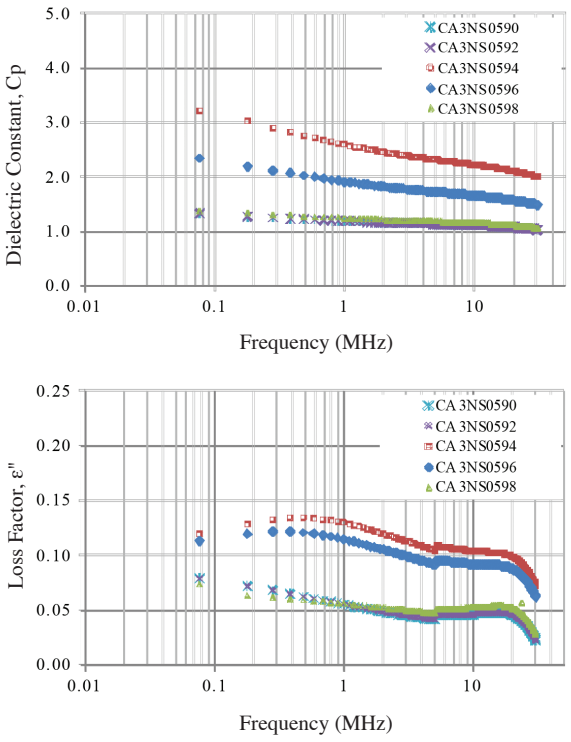

FIGURE 4. Dielectric properties of chitosan membrane varying NR content

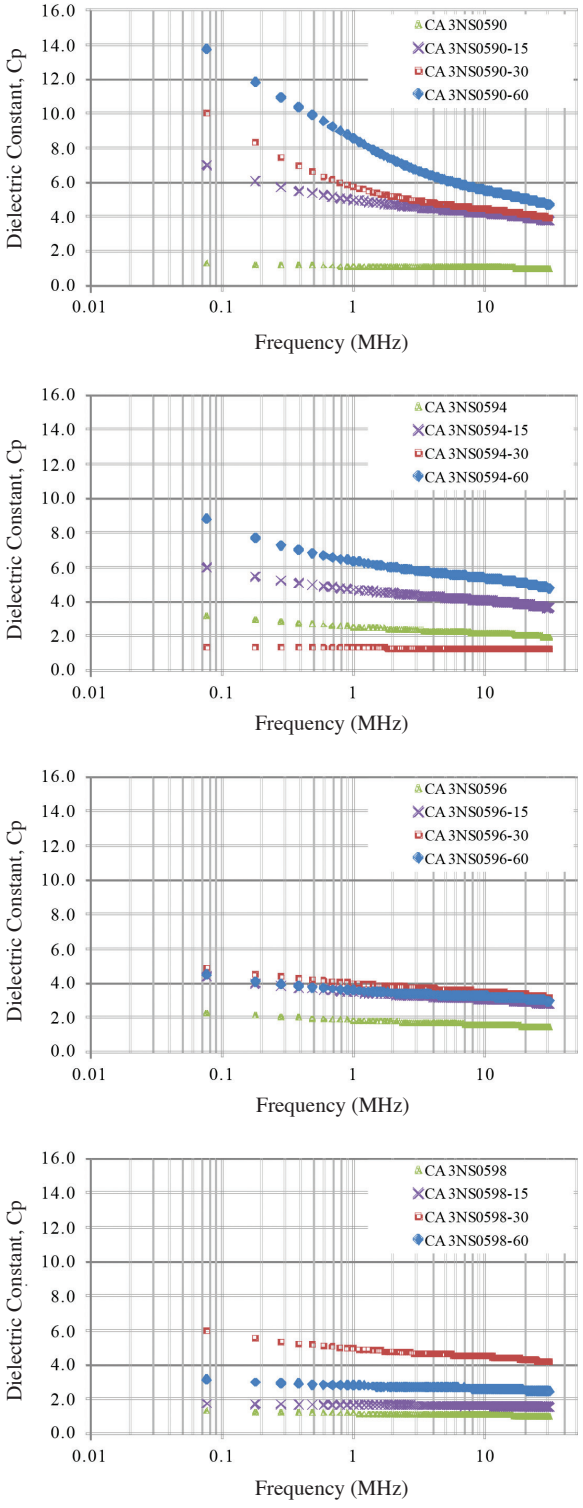

FIGURE 5. Dielectric properties of polymer films after surface treatment with sulfuric acid

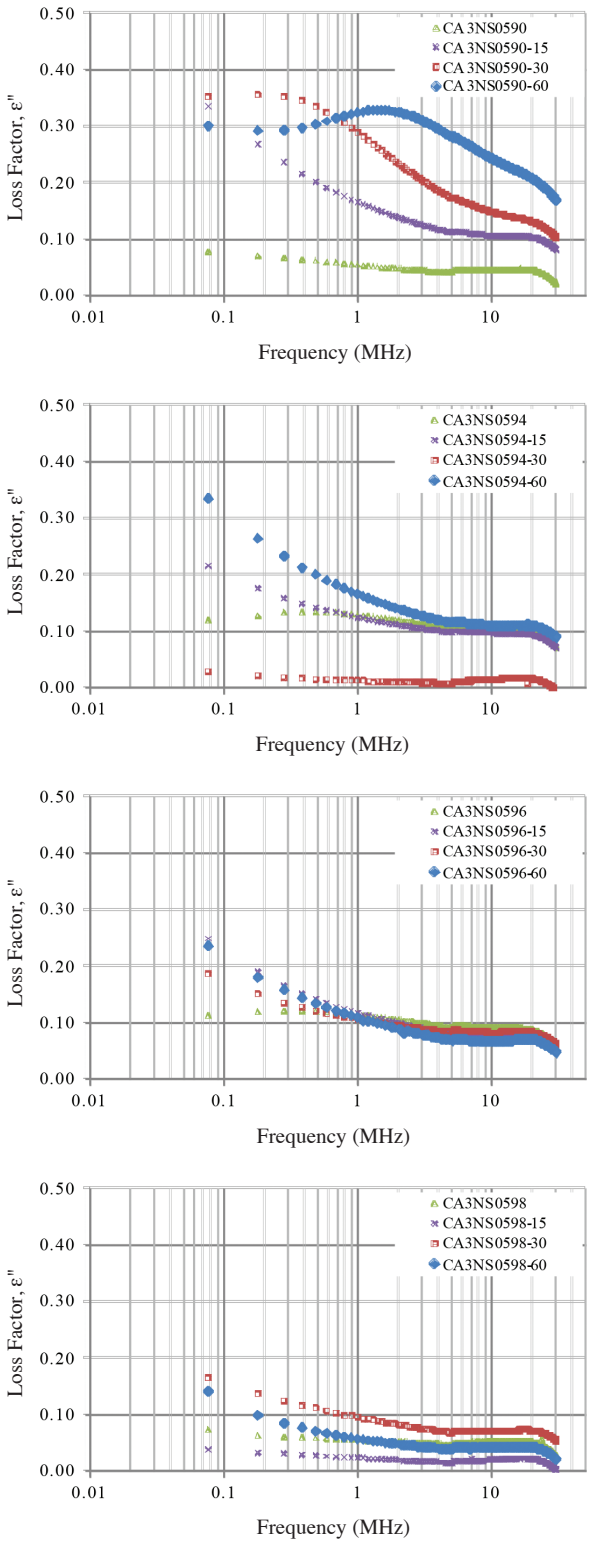

FIGURE 6. Dielectric loss of polymer films after surface treatment with sulfuric acid

The dielectric properties of polymer films with lower concentration of NR were not changed with increasing time of immersing time.

CONCLUSION

The membrane obtained from the incorporation of chitosan with NR was found that the mechanical property is improved. The dielectric constant revealed with interfacial polarization and conductivity of polymer film is mainly changed with NR content. NR film was formed and covered chitosan particle and degraded after immersing in sulfuric acid. The sulfonate ionic interaction between NR and sulfate group was observed by dielectric measurement.

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REFERENCES

Clarizia, G., Algieri, C. & Drioli, E. 2004. Filler-polymer combination: A route to modify gas transport properties of a polymeric membrane. *Polymer* 45: 5671-5681.

Ismail, H., Shaari, S.M. & Othman, N. 2011. The effect of chitosan loading on the curing characteristics, mechanical and morphological properties of chitosan-filled-natural rubber (NR), epoxidised natural rubber (ENR) and styrene-butadiene rubber (SBR) compounds. *Polymer Testing* 30(7): 784-790.

Kittur, A.A., Kulkarni, S.S., Aralaguppi, M.I. & Kariduraganavar, M.Y. 2005. Preparation and characterization of novel pervaporation membranes for the separation of water-isopropanol mixtures using chitosan and NaY zeolite. *Journal of Membrane Science* 247: 75-86.

Sapuan, S.M., Mustapha, F., Majid, D.L., Leman, Z., Ariff, A.H.M., Ariffin, M.K.A., Zuhri, M.Y.M., Ishak, M.R. & Sahari, J. 2011. The effect of chitosan loading on the properties of chitosan filled epoxidized natural rubber compound. *Key Engineering Materials* 851: 471-472.

Wanichapichart, P., Sungkum, R., Taweepreeda, W. & Nisoa, M. 2009. Characteristics of chitosan membranes modified by argon plasmas. *Surf. Coat. Technol.* 203(17-18): 2531-2535.

White, J.C., Dutta, P.K., Shqau, K. & Verweij, H. 2010. Synthesis of ultrathin zeolite Y membranes and their application for separation of carbon dioxide and nitrogen gases. *Langmuir* 26(12): 10287-10293.

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